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## ON THE DISSOLUTION PROPERTIES OF GaAs IN Ga

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Space Sciences Laboratory

January 1977



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*George C. Marshall Space Flight Center  
Marshall Space Flight Center, Alabama*

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16. ABSTRACT  The dissolution of GaAs in Ga was studied to determine the nature and cause of faceting effects. Ga was allowed to dissolve single crystalline faces under isothermal conditions. Of the crystalline planes with low number indices, only the (100) surface showed a direct correlation of dissolution sites to dislocations. The type of dissolution experienced depended on temperature, and there were three distinct types of behavior.					
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## ON THE DISSOLUTION PROPERTIES OF GaAs IN Ga

### INTRODUCTION

There are several important technical processes in which dissolution plays a significant role. In some cases dissolution produces an unavoidable negative effect, while in others it is used as a means of producing polished flat surfaces or removing material in a controlled manner. Further, dissolution and its counterpart, precipitation, are utilized in materials processing techniques such as single crystal growth and purification.

There are several distinct types of dissolution, generally characterized by the manner in which the solvent and solute interact in the liquid state (see, for example, Reference 1). The most common is polar dissolution, with water being the most important solvent of this type. Compare, for example, the dielectric constant of water (78.5 at 25°C) with ethyl alcohol (24.3 at 25°C). Other types of dissolution do not depend on the polar properties of the solvent and/or solute as is the case for metallic systems. The subject of this report is the dissolution of a semiconductor by a metal solvent, in particular GaAs in Ga. Liquidus solubilities of GaAs in Ga have been reported [2 - 5] but only in regard to bulk rates. This report is concerned with the detailed nature of a dissolving single crystalline substrate of GaAs in Ga.

The results reported herein represent part of a larger study on liquid phase epitaxial growth of GaAs from liquid Ga. Poor growth habit was encountered in the study, especially with the thermal gradient method. Several possible causes were considered, including bulk convection and dissolution irregularities. The object of the investigations reported herein was to determine the cause of faceted dissolution pits on GaAs surfaces undergoing dissolution in Ga. These results would hopefully determine conditions to eliminate or minimize the deterioration of the substrate prior to growth due to dissolution.

There are a number of possible causes of faceted dissolution; e.g., the pits may be nucleated at (1) dislocation sites, (2) kink sites, and (3) impurity sites, etc. Pit nucleation at sites where dislocations outcrop on the surface was thought to be the most likely mechanism.

## EXPERIMENTAL PROCEDURE

Undoped wafers with (111), ( $\bar{1}\bar{1}\bar{1}$ ), (110), and (100) surface orientations were cut from a GaAs boule obtained from Wacker-Chemie. Carrier concentration of the material was typically  $8 \times 10^{15}/\text{cm}^3$ . The Ga used for dissolution was supplied by Apache Chemicals with a stated purity of 99.999 percent. Reagent grade chemicals were used for the chemical polishes and etchants. The hydrogen for cleaning was 99.996 percent pure.

The wafers were mechanically polished with alumina using a final grit size of  $0.05 \mu\text{m}$ . This was followed by a chemical polish of  $3\text{HNO}_3:1\text{HF}:2\text{H}_2\text{O}$  at room temperature. All orientations except (111) were also polished for 2 to 3 min in a 10 percent bromine/methanol solution at room temperature. The preferential etchant used for the (111), ( $\bar{1}\bar{1}\bar{1}$ ), and (110) surfaces was  $1\text{HNO}_3:3\text{H}_2\text{O} + 1$  percent  $\text{AgNO}_3$ . For the (111) surfaces the etchant was used at room temperature, while for the ( $\bar{1}\bar{1}\bar{1}$ ) and (110) orientations, temperatures in excess of  $80^\circ\text{C}$  were necessary. The (100) surfaces were etched in molten KOH.

To ensure good contact during dissolution, the GaAs and Ga were initially placed in separate compartments in a quartz container or boat. The boat was then placed inside a quartz tube furnace and brought to a temperature of  $600^\circ\text{C}$  under a hydrogen atmosphere. The furnace was then allowed to cool to the desired temperature and "tipped," resulting in the Ga flowing over the GaAs surface. This "tipping" technique allowed a surface scum on the liquid Ga to be broken and the GaAs surface to be covered with clean Ga. A Ga surface scum was present at temperatures above approximately  $500^\circ\text{C}$ , independently of how the hydrogen was treated prior to entering the furnace. In all results reported here, the hydrogen was passed through a liquid nitrogen trap and the tipping technique was employed.

## RESULTS

It was found that individual etch pits on the (111) faces were not reproducible; i. e., when an etched surface was mechanically polished, then chemically polished, and again etched, the original etch pits were not reproduced. While individual etch pits were not reproducible on ( $\bar{1}\bar{1}\bar{1}$ ) surfaces, general patterns were reproducible. As a result of this irreproducibility, the following

procedure for correlating the Ga dissolution pits with dislocation etch pits was adopted. The crystals (111) and ( $\bar{1}\bar{1}\bar{1}$ ) were acid etched until well-defined etch pits appeared. These were then dissolved in Ga at a temperature of 350°C for 5 min. No correlation between the etch pits and the dissolution facets could be found; see, for example, Figure 1.

Since no correlation could be found between dislocations and dissolution facets, it was thought that the latter could possibly be nucleated at sites where atoms or ions were adsorbed on the surface. Accordingly, solutions of  $\text{Fe}^{3+}$ ,  $\text{Ag}^+$ , and  $\text{Cu}^{2+}$  ions, each with concentrations of 10, 100, and 1000 ppm, were prepared. The ( $\bar{1}\bar{1}\bar{1}$ ) surfaces were used for this experiment because positive ions are more likely to be adsorbed on the negative As surface than on the positive Ga (111) surface. Part of the surface was covered with silicone grease, and the other part was covered with one of the ion solutions (for 5 min). The ion solution was then washed off with distilled water, the silicone grease was removed with trichloroethylene, and the crystal was dissolved in Ga at 350°C for 5 min. Microscopic examination showed that the same number of dissolution pits formed on both regions of the surface. This was the case for the three ions studied, at their highest concentrations; see, for example, Figure 2.

The dissolution behavior of (110) and (100) surfaces was also studied. In the case of (111) and ( $\bar{1}\bar{1}\bar{1}$ ) surfaces, the faceted dissolution pits were hexagonal or trigonal in shape, whereas for (110) and (100) surfaces, they were rectangular or square.

No correlation between dislocation etch pits and dissolution pits could be found for (110) surfaces (Fig. 3).

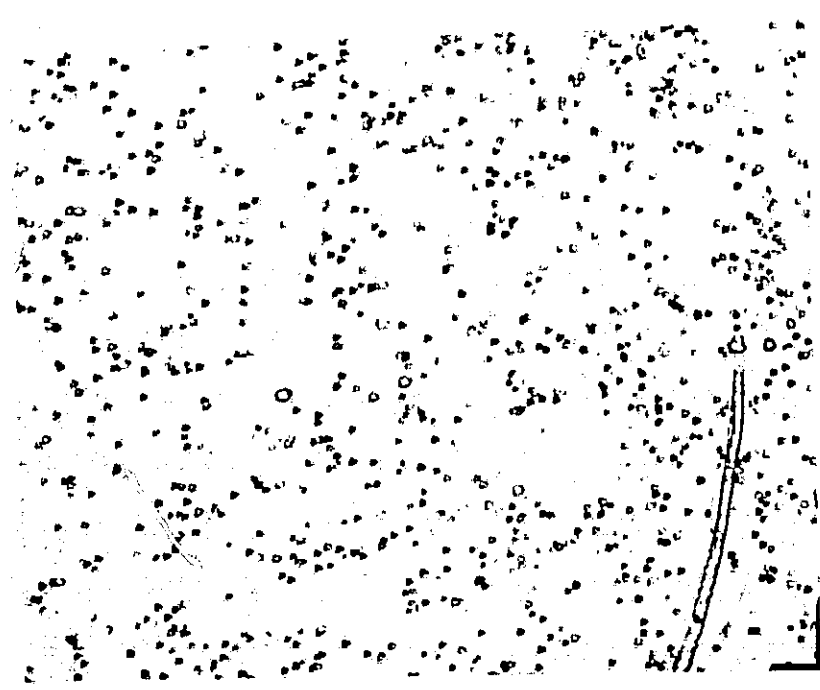
In the case of (100) surfaces, however, very good correlation was evident. As can be seen from Figures 4 and 5, each etch pit becomes the site of a Ga dissolution pit.

An attempt was also made to measure the kinetics of dissolution of GaAs in Ga metal. It was hoped to determine the rate of dissolution as a function of temperature, calculate an "activation" energy for the dissolution of each orientation, and determine the relative reactivity of each orientation. Three separate procedures were used in this attempt as follows:





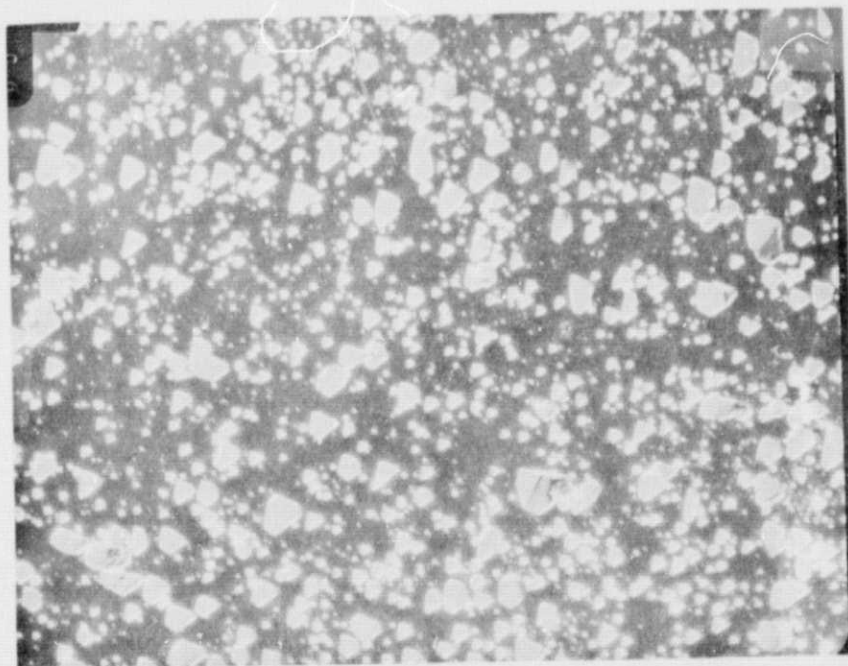
b. Ga etched.



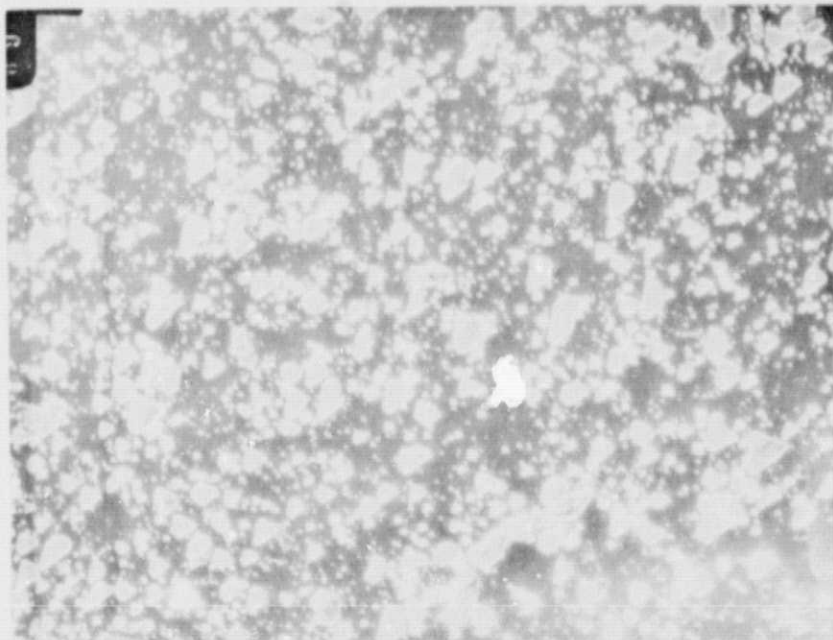
a. Acid etched.

Figure 1.  $(\bar{1}\bar{1}\bar{1})$  surface (80X).

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a. Section of surface covered with Ag<sup>+</sup> ions.



b. Section of surface protected by silicone grease.

Figure 2.  $(\bar{1}\bar{1}\bar{1})$  surface (400X).

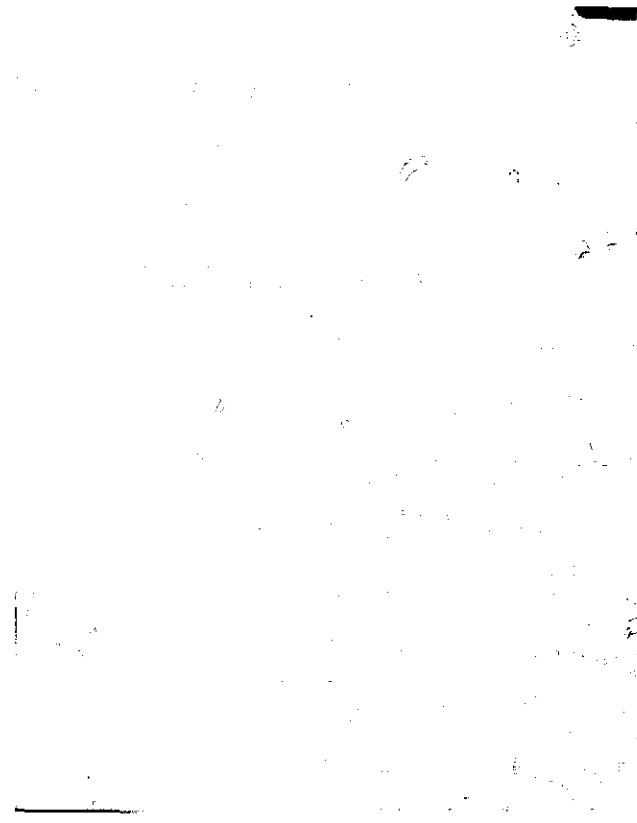
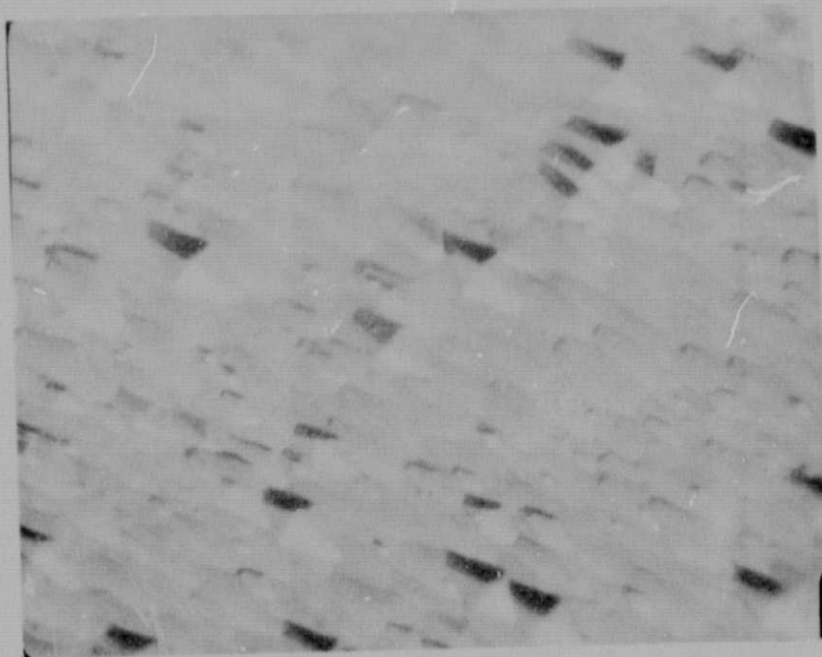


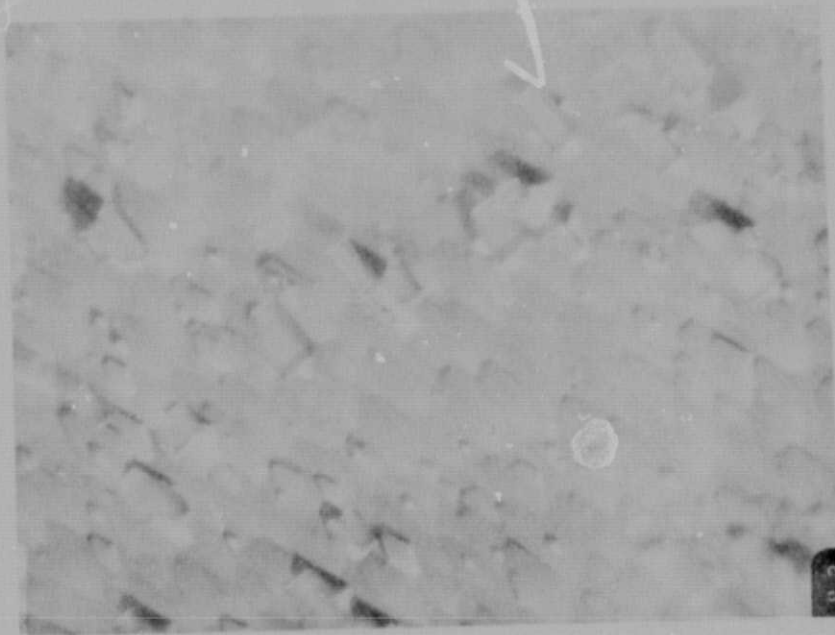
Figure 3. (110) surface (400X); acid etched,  
with subsequent dissolution in Ga.

1. Calorimetric method — This method made use of a differential thermal analyzer (DTA), and it was hoped to measure the change in heat capacity with time as dissolution proceeded. This proved impossible because the DTA was unable to detect the very small changes (if there were any) involved, and the method was abandoned.

2. Gravimetric method using a Czochralski crystal puller — The loss in weight of a GaAs crystal was to be measured as a function of time of dissolution. A specially constructed quartz crystal holder was attached to the pulling rod of a Czochralski crystal puller. A hydrogen ambient was maintained, and the rear face and sides of the GaAs dice ( $3.8 \times 3.8$  mm) were coated with a chemical deposit of  $\text{SiO}_2$  to protect them from dissolution. The Czochralski chamber was heated to  $600^\circ\text{C}$  to clean the crystal surface of reducible impurities and then cooled to the required temperature. When the temperature had stabilized, the



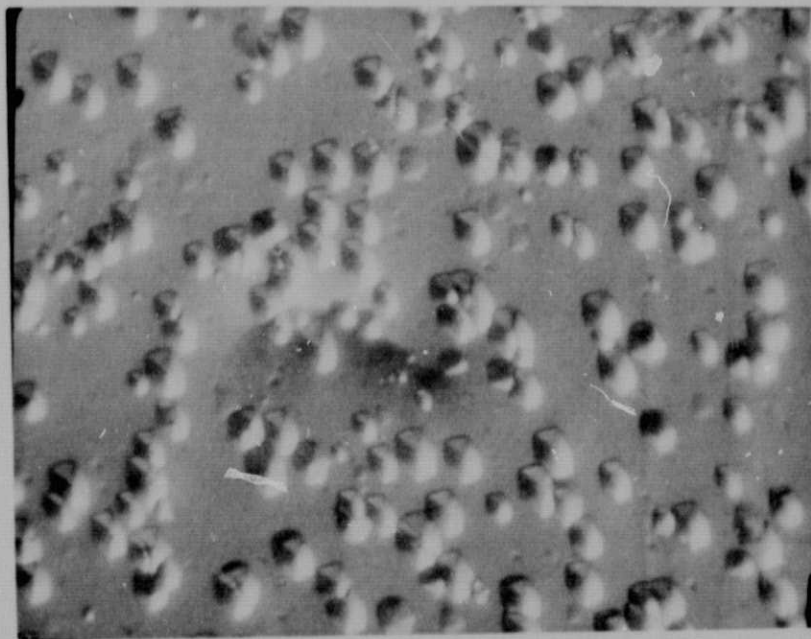
a. Etched in molten KOH for 50 s.



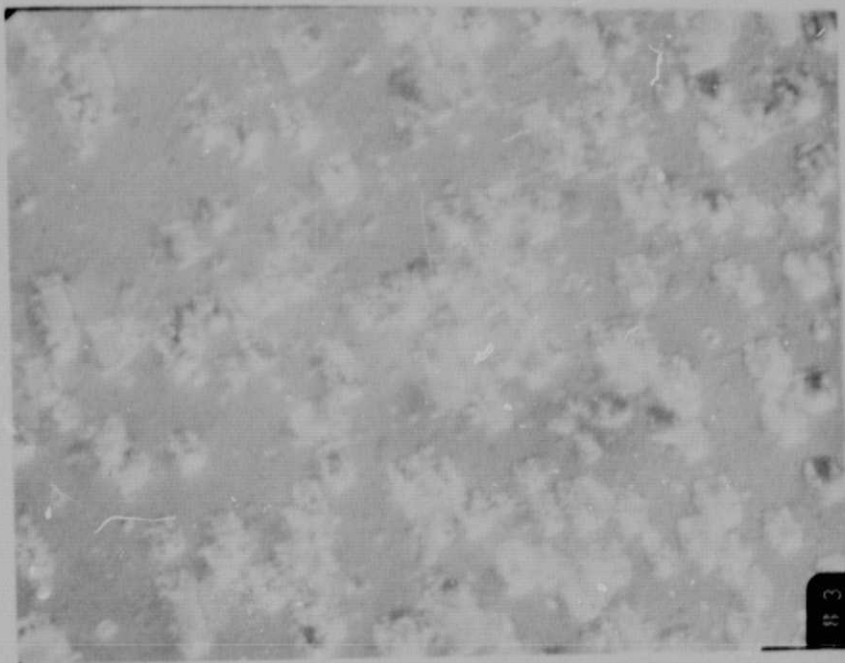
b. Subsequent Ga dissolution.

Figure 4. (100) surface (1600X).

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a. Etched in molten KOH for 25 s.



b. Subsequent Ga dissolution.

Figure 5. (100) surface (1600X).

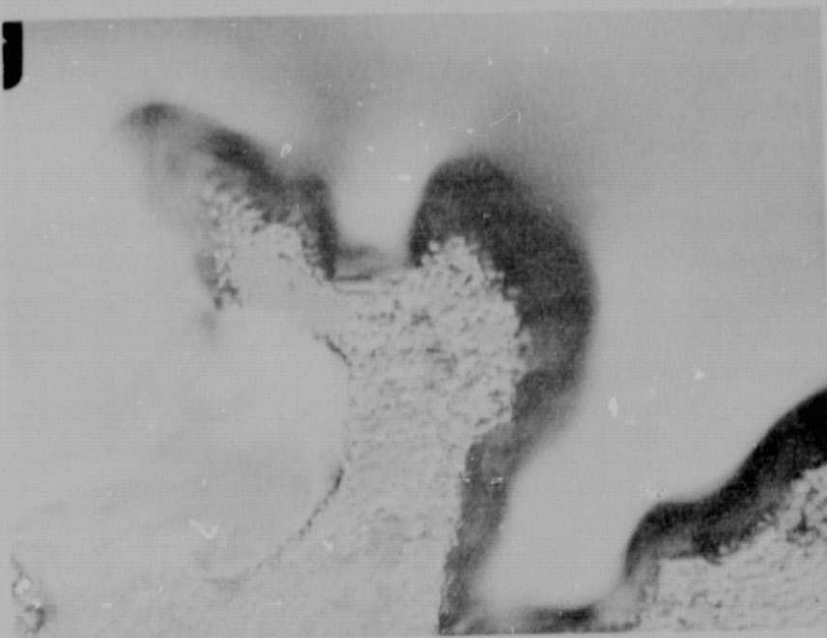
crystal was lowered into the Ga, allowed to remain there for a given time interval, and then rapidly removed. This procedure offered very good control over the time measurements. However, it was found that the crystal did not wet uniformly because it was unable to fully break through the Ga surface scum, and this method was also abandoned.

3. Gravimetric "tipping" method — This method is as described previously for the pitting experiments. The Ga was tipped onto the GaAs dice after hydrogen cleaning at 600°C and cooling to the required temperature. The furnace tube and boat were removed from the furnace after a given time interval, and the GaAs crystal was removed and weighed. Ga adhering to the surface of the crystal was removed by dissolution in concentrated HCl before weighing. This procedure was repeated for varying time intervals and at temperatures ranging from 350° to 600°C; the loss in weight of the GaAs with time was the rate of dissolution at the particular temperature used. Fresh Ga (3 g) was used for each data point. Problems again arose. Below 500°C the solubility of GaAs in Ga was so low (4 mg per 3 g of Ga) that serious errors were introduced in the weighing, with consequent irreproducibility in the results. At and approaching 600°C, the surface became very unevenly attacked by the Ga (Fig. 6). This unevenness or roughing of the surface occurred on a macroscopic scale and is quite different from the microscopic pitting observed at lower temperatures. It seems unlikely that uneven wetting is responsible for this, because those portions of the surface which are in relief have in fact been wetted and dissolved to some extent [Fig. 6 (b)]. Further, no such uneven wetting was observed at lower temperatures. Possibly convection currents are removing GaAs away from the surface in an uneven manner, and since mass transport of GaAs from the surface controls the rate of dissolution at these temperatures (see the following paragraph), this would account for the unevenness of the dissolution.

One interesting item of information that emerged from these kinetic experiments was that the kinetically controlling step of the dissolution is temperature dependent. At low temperatures (approximately 350°C) dissolution pits appeared on all faces examined, indicating that an "activation" energy barrier is controlling the rate of dissolution. At higher temperatures (approximately 500°C) all the surfaces became smooth and polished, indicating that diffusion of GaAs away from the surface had become the controlling factor. At 500°C the mass transport of GaAs from the surface was very even, with a resulting polishing effect; uneven mass transport, as reported previously, did not occur until temperatures of 600°C were used. The temperature at which the changeover from activation to diffusion control occurred varied with surface orientation. For (111) surfaces the change occurs at approximately 400°C



a. 80X.



b. 400X.

Figure 6. (100) surface; dissolved in Ga at 600°C.

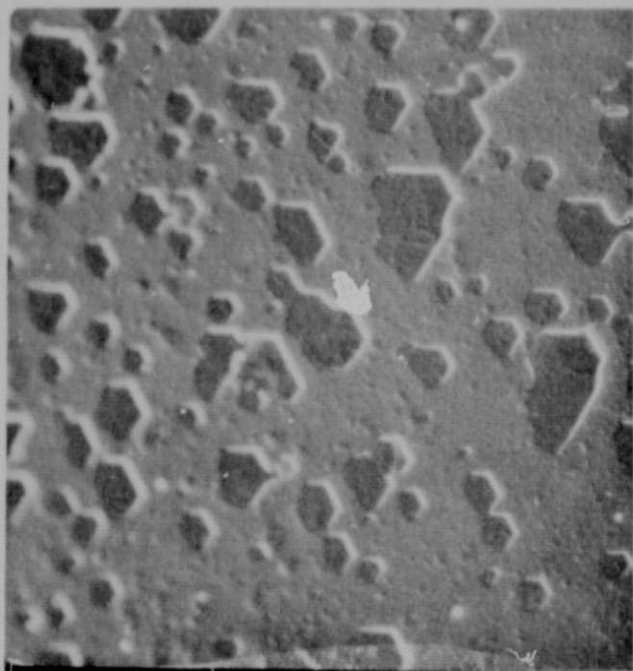
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(Fig. 7); on (111) surfaces it occurs between 400° and 450°C (Fig. 8); and on (110) and (100) surfaces it occurs between 450° and 500°C (Figs. 9 and 10). Crystals immersed in Ga at 300°C and brought rapidly (9 to 12 min) to 500°C and immediately removed still had deep dissolution pits remaining on the surface (Fig. 11), whereas those held at the higher temperature for several minutes became polished. This is significant in the area of epitaxial growth since, if the seed crystal can be held at temperatures less than approximately 550°C for several minutes in undersaturated Ga, a smooth surface is obtained; subsequent growth should then give a uniformly thick epilayer.

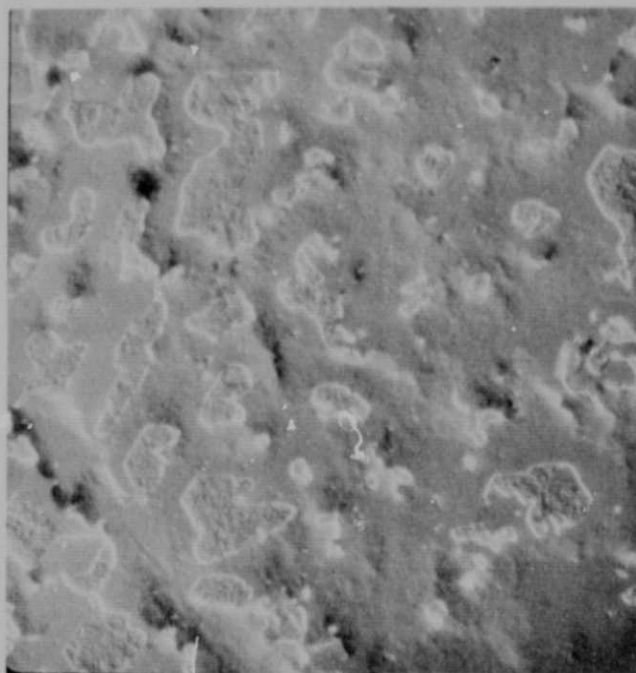
## CONCLUSION

The detailed nature of the dissolution of single crystalline GaAs by Ga was found to depend on temperature as well as substrate orientation. The transition temperature from surface kinetic controlled to diffusion controlled dissolution was different for the (111),  $\overline{1}\overline{1}\overline{1}$ , (110), and (100) surfaces. At higher temperature the dissolution was found to be macroscopically irregular even under isothermal conditions. This is attributed to fluid motion near the dissolving interface and, as such, should be gravity dependent.

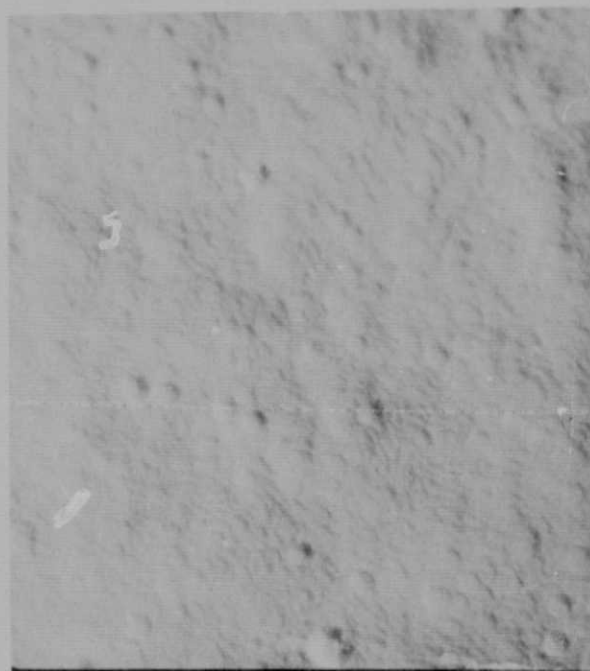




a. Ga dissolved at 350°C for 5 min.

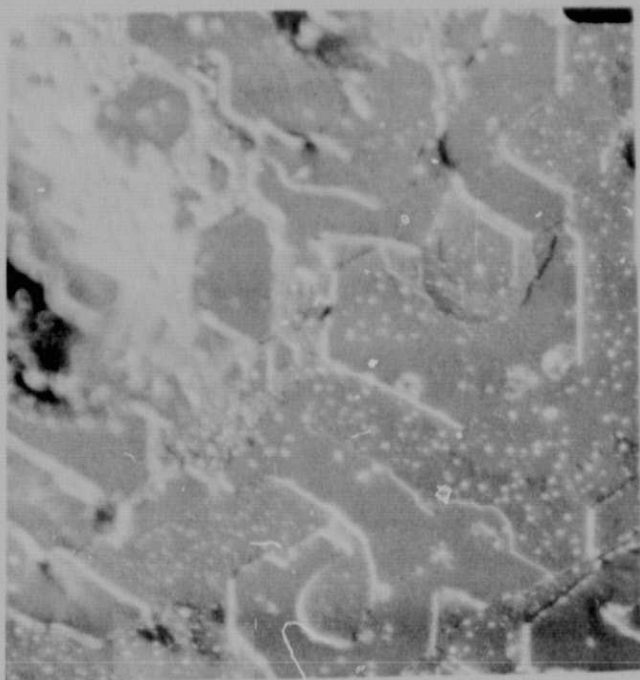


b. Subsequent to a., Ga dissolved at 400°C for 5 min.



c. Subsequent to b., Ga dissolved at 450°C for 5 min.

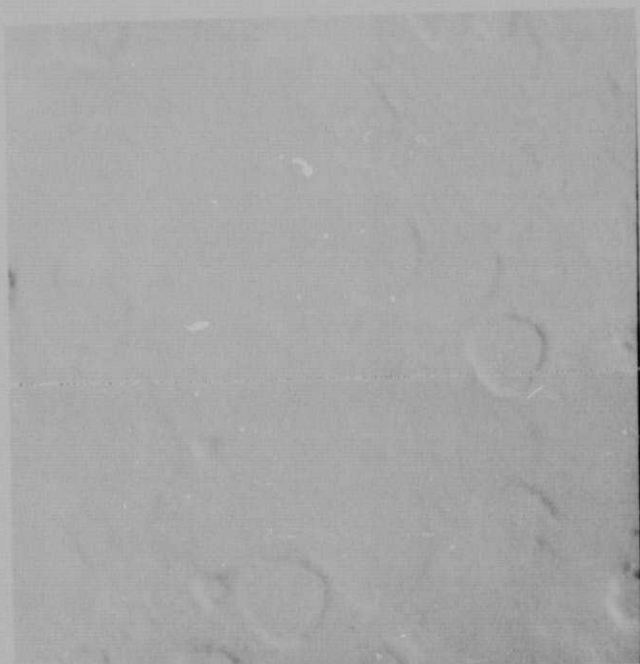
Figure 7.  $(\bar{1}\bar{1}\bar{1})$  surface (800X).



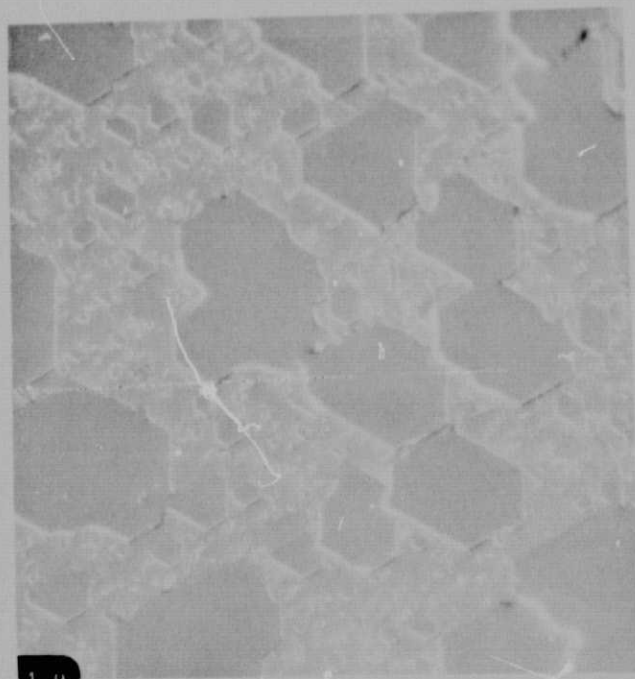
a. 400°C.



b. 450°C.



c. 500°C.

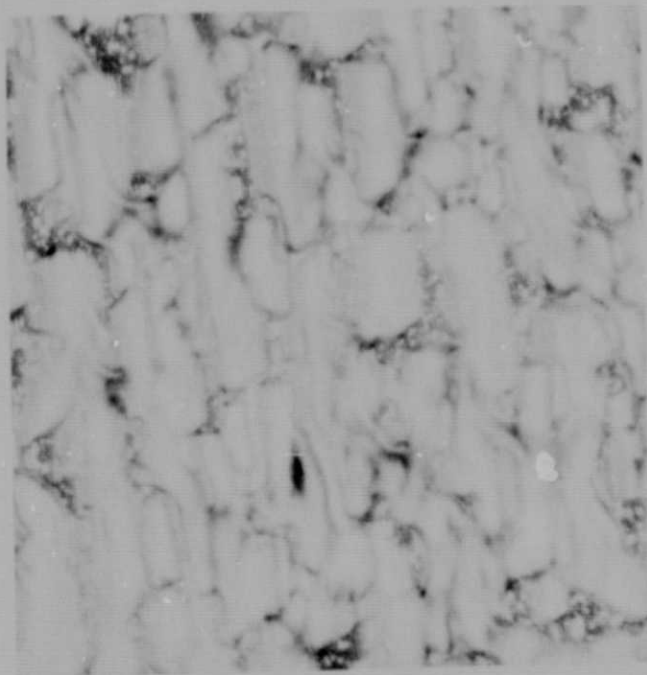


d. 350°C.

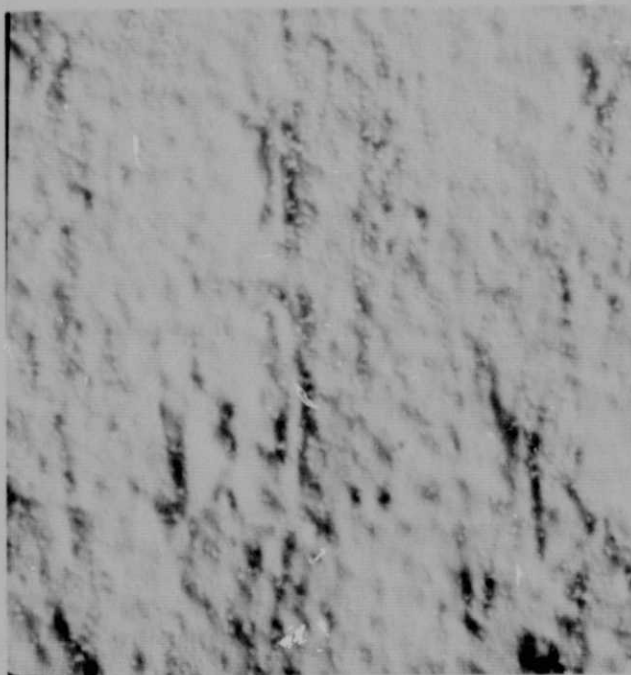
Figure 8. (111) surface (800X); Ga dissolved in sequence for 5 min at temperatures shown.



a. 400°C.

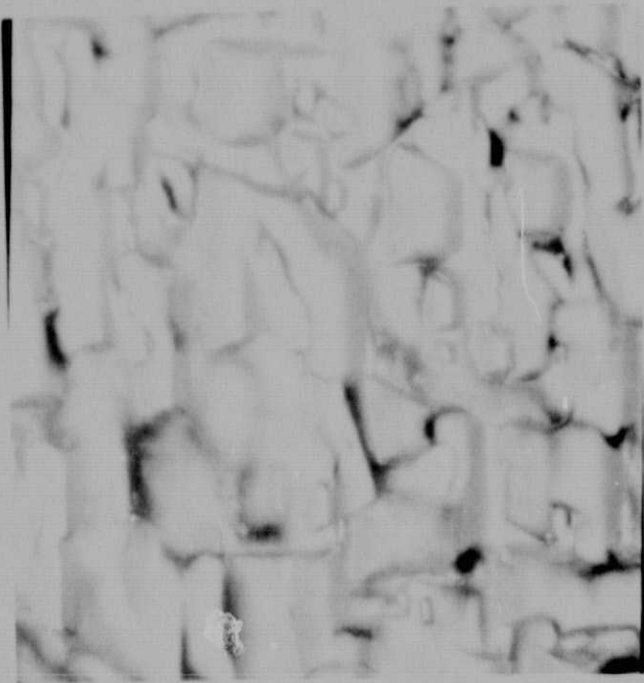


b. 450°C.

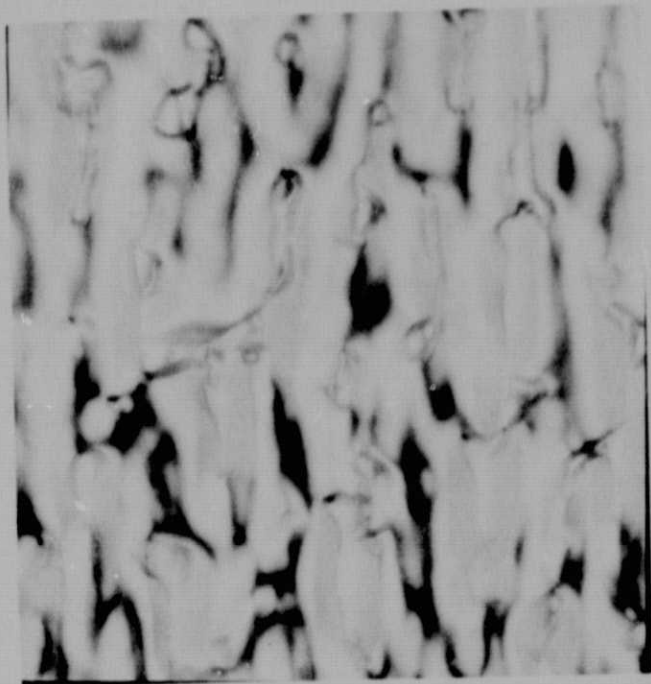


c. 500°C.

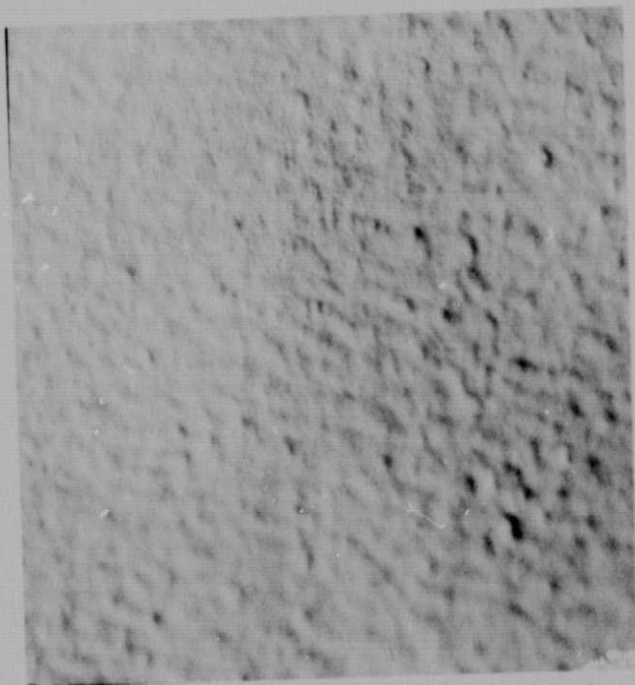
Figure 9. (110) surface (800X); Ga dissolved in sequence for 5 min at temperatures shown.



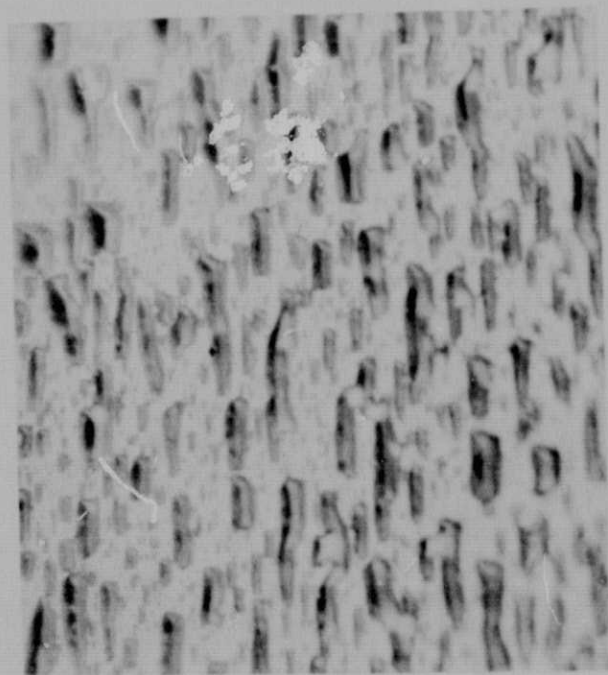
a. 400°C.



b. 450°C.

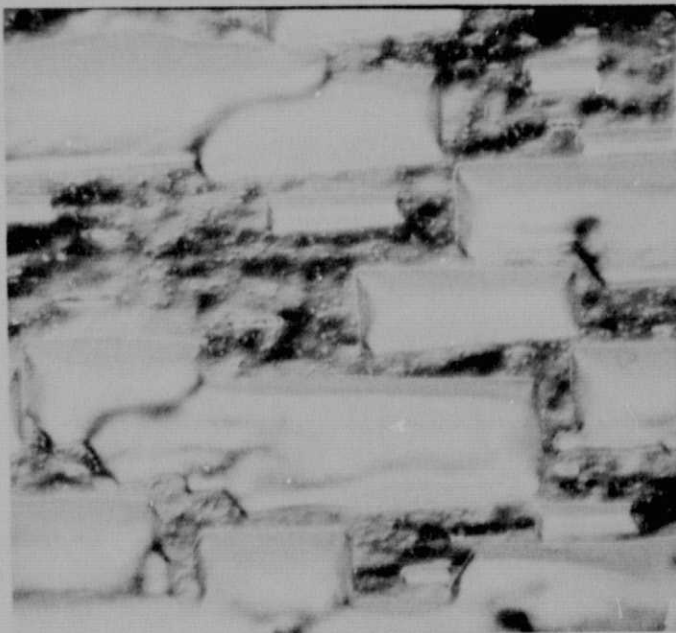


c. 500°C.



d. 350°C.

Figure 10. (100) surface (800X); Ga dissolved in sequence for 5 min at temperatures shown.



a. Immersed in Ga at 300°C and brought to 500°C over period of 12 min and removed; pits are 6.2  $\mu\text{m}$  deep.



b. Brought from 300°C to 500°C over 9 min, and allowed to remain at 500°C for 6 min and removed.

Figure 11. (110) surface (800X).

## REFERENCES

1. Fleck, G.: *Equilibria in Solution*. Holt, Rinehart and Winston, Inc., 1966.
2. Köster, W. and Thoma, B.: *Z. Metallk.*, vol. 46, 1955, p. 291.
3. Van der Boomgaard, J. and Schol, K.: *Philips Research Reports*, vol. 12, 1957, p. 127.
4. Hall, R. N.: *J. Electrochemical Society*, vol. 110, 1963, p. 385.
5. Rubenstein, M.: *J. Electrochemical Society*, vol. 113, 1966, p. 752.



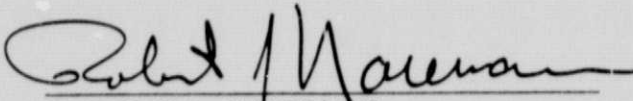
## APPROVAL

### ON THE DISSOLUTION PROPERTIES OF GaAs IN Ga

By M. C. Davidson and A. H. Moynahan

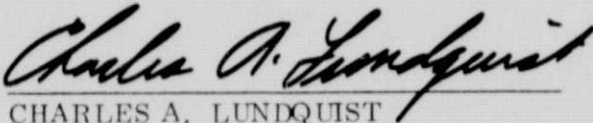
The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.



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